Permeselectives Properties Measurements of Low Density Polyethylene

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Abstract: On a fundamental level, the transition temperature (Tg) marks the transition from a cooperative mobility (T > Tg, rubbery state) to a localized mobility (T < Tg, glassy state). Fickian diffusion in polymers is an idealized case of mass transport, corresponding to a free diffusion of permeant without interactions with the molecular conformation of the polymer and then with its structural relaxation. There is a direct relationship between the diffusion and relaxation of the polymer and on whether we place ourselves below (glassy state) or above (rubbery state) of the glass transition temperature Tg, the diffusion mechanisms are very different. There are two types of models to describe the variation of the diffusion coefficient D. In this contribution, we will review the different behaviors of the distribution function of the Tg and show us the Deborah number D - α defined as the ratio of characteristic times of diffusion and relaxation, to indicate the nature of dissemination and to apply the model. As a practical example we have studied the case of low density polyethylene manufactured and processed by the national Algerian plastic society ENPC.

Key words: Diffusion · Permeation · Polyethylene

INTRODUCTION

The permeation of a permeant through a polymer occurs following 3 steps: the sorption of permeant, its diffusion through the polymeric film and desorption on the other side of the film.

The diffusion theory is based on the assumption that the flux of material diffusing per unit area and time through a substance is proportional to the concentration gradient.

In the case of a steady state, this relationship led to the first Fick’s law:

\[ j = -D \frac{\partial C}{\partial x} \]  

(1)

The case of unsteady flow (where the concentration gradient depends on the time) is described by Fick’s second law:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  

(2)

The solution of the Fick equation has been the subject of many studies and in many cases the object of interest is the mass fraction Mt of absorbed substance inside the polymer:

\[ M_t = \int_{-\infty}^{+\infty} C dx \]  

(3)

C is the concentration in an elementary layer dx at an abscissa x.

The kinetics of sorption of a polymer can be expressed by:

\[ \frac{M_t}{M_{\infty}} = k t^n \]  

(4)

Mt: mass fraction of absorbed substance

M_\infty: Quantity of absorbed substance at equilibrium

k: Constant

n: Parameter that varies depending on the mode of sorption

n = \frac{1}{2} defined type I sorption that occurs when the system polymer / permeant obeys to a Fickian diffusion. The sorption rate does not depend on the speed of swelling of the polymer [1].

Type II sorption corresponds to n = 1. This mode of sorption occurs when the rate of diffusion of permeant molecules is greater than the rate of relaxation of polymer chains. This kind of behavior (non Fickian) corresponds...
to the behavior of organic vapors in glassy polymers. The kinetics of sorption is highly dependent on the rate of swelling of the polymer [2].

The case when \( n \) is between \( \frac{1}{2} < n < 1 \) is called the non-Fickian sorption. It occurs when the rate of diffusion of permeant molecules is of the same order as the relaxation rate of the polymer. However, no current theory is able to adequately explain this behavior [3].

When the permeant molecules do not interact with the polymer (the case of simple gases) the diffusion coefficient \( D \) is constant. But otherwise, the diffusion coefficient \( D \) is dependent on several factors.

The first distribution will depend on the nature of the polymer, the mobility of its chains, the degree of cross linking, the degree of crystallinity, etc. The glass transition temperature is a parameter that describes fairly thoroughly the nature of the polymer, because it marks the transition from a localized mobility (\( T < T_g, \) glassy state) to a cooperative mobility (\( T > T_g, \) rubbery state).

Using Deborah number (\( \omega_d \)) to describe diffusion in polymers was proposed by Vrentas et al. [4] and [5], in fact it is the ratio between the duration of the experiment reported in the lifetime of the observed phenomenon. The glass transition is defined by a number of Deborah equal to 1.

For different polymers, it was found that the diffusion coefficient increases with decreasing the glass transition temperature. This is illustrated by the (Fig. 1) obtained by Brown et al. [6].

Solving Fick's differential equation for the steady state allows access to the coefficient \( D_L \) (cm\(^2\)/s) from the equation:

\[
D_L = \frac{L^2}{6t_L}
\]

Where \( L \) is the film thickness in cm and \( t_L \) the time lag in seconds.

A second method for determining the diffusion coefficient can be used. It is based on the inflection point \( I \) of the permeation curves corresponding to a time \( t_{0.24} \) and a value of \( J/J_0 = 0.24 \):

\[
D = \frac{0.091L^2}{t_{0.24}}
\]

Permeation is the penetration of the permeate through the polymer and is related to a material's intrinsic permeability.

The process used leads directly to an accumulated quantity of permeant \( Q \) (time-lag method) or the transfer rate \( dQ/dt \) (differential permeation). The study of establishment and access to the steady flow can directly obtain the diffusion coefficients \( D \) and permeation \( P \). The solubility coefficient \( \sigma \) can then be deduced.

**MATERIALS AND METHODS**

To carry out our measurements, we have been led to use the permeation and diffusion device developed in the BPM laboratory (UMR 6522, CNRS), University of Rouen (France). This instrument is extensively described in the work of S. Marais et al. [7, 8, 9].

Low-density polyethylene films were obtained by extrusion of granules supplied by Skikda-ENIP Company (reference B24/2, east Algeria). The density (d) and melt index (Mi) given by the supplier are respectively \( d = 0.923 \) and \( Mi = 0.3 \) g/min. This extrusion performed at ENPC-Chief Company (west Algeria) leads to the formation of films.

The measurement method assumes that the flux \( J \) (L, t) through the dry surface can be expressed by:

\[
J(L,t) = \frac{f}{A}10^6 \frac{p_{in} - p_{out}}{RT_r} \cdot p_t
\]

Where:

- \( A \) : Area of exposed film (30 cm\(^2\))
- \( R \) : Perfect gas constant (0.082-atm.cm\(^3\).K\(^{-1}\).mmol\(^{-1}\))
- \( T_r \) : Temperature of experiments in K.
- \( f \) : Dry gas flow cm\(^3\).s\(^{-1}\).
- \( x_{in} \) and \( x_{out} \) : Concentrations at the inlet and outlet gas sweep ppmV.
- \( p_t \) : Total pressure (1 atm).
- \( J(L, t) \) : Flux mmol.cm\(^{-2}\).s\(^{-1}\).

\( X_{in} \) concentrations and \( X_{out} \) are obtained directly to oxygen and indirectly to water from the dew point of the sweep gas.
From the steady state it is then possible to determine the permeability $P$ of the film:

$$P = \frac{J_{st} L}{\Delta a} \quad (8)$$

With $J_{st}$: Steady flow

$\Delta a$ : Difference in activity between the two sides of the film

The expression of the normalized flux variation $JL$ according to the reduced quantity $t/L^2$ allows to standardize the quantities involved on the one hand and to ignore the sample thickness $L$ on the other.

For water permeation study, the sample is first stored in a vacuum dryer for at least 12 hours at room temperature. It is then inserted into the measuring cell. A purge is then performed to dry up the film and the cell by the scans of ultra pure nitrogen (Cell downstream: receptor compartment) and pure (Upstream cell: donor compartment). The average thickness is obtained from 21 measurements with a micrometer (ROCH 0-25) in different parts of the sample surface.

The flow of purge gas is fixed at 3.3 cm$^3$/s during the first ten hours of drying, then to 9.3 cm$^3$/s until the signal stabilizes (dew point below -68°C).

After closing the nitrogen supply, the donor compartment is then quickly fed with pure liquid water. The filling time is very short, about 30 seconds and can be neglected at the time required to obtain the steady state.

The experiment consists in the acquisition and recording, with time, the following measures:

- Dew point temperature $T_r$ (Shaw)
- Dew point temperature $T_r$ (mirror)
- Cell temperature
- Relative Humidity

Experimentally, increasing the dew point temperature $T_{r}$ of dry gas, corresponding to its enrichment moisture is recorded as a function of time until the steady state.

The frequency in data acquisition is 1 point every 10 seconds.

After grading, shaping and fitting the two initial curves, obtained from the two probes, we obtain a single curve that will benefit from the qualities of each hygrometer: the speed of the capacitive probe (transient state) and precision of the probe mirror (initial state and steady state).

The experimental curves, as shown in the figure (Fig. 2) show three characteristic zones:

- A significant flow for an hour or more (priming regime).
- An increasing flow for several hours (setting regime).
- A constant flow (steady state).

The priming time and duration of scheme property are directly related to the diffusivity of water in the polymer.

**RESULTS AND DISCUSSION**

The experimental results obtained on the permeameter for different polymers are presented on the (Table 1).

The permeability values ranged from $0.42 \times 10^{-9}$ mmol.cm$^{-1}$.s$^{-1}$ (Polyimide) and $37.6 \times 10^{-9}$ mmol.cm$^{-1}$.s$^{-1}$ (Polyethersulfone) or 40 to 4000 Barrer.

The diffusion coefficient $D_i$ varies from $0.1 \times 10^{-5}$ cm$^2$.s$^{-1}$ (Polyimide) to $7.42 \times 10^{-5}$ cm$^2$.s$^{-1}$ (Polyethylene). LDPE, semi-crystalline polymer, with a particular molecular structure is characterized by the lowest quantity of sorbed water. This result is certainly due to the highly hydrophobic nature of low density polyethylene.

The permeation coefficients are measured when the regime is fully established; the variations of this property are less pronounced than those of diffusion. However, the neutral LDPE ($P = 32$ Barrer) appears to be less permeable than stabilized LDPE ($P = 43$ Barrer), these results are presented in the table (Table 2).

A comparison with bibliographic data allows us to situate our results, for comparable experimental conditions. Table (Table 2) allow verifying the consistency of the magnitude of values.

Literature data given in (Table 2) showed that apart from the value of $0.31$ g.mm.m$^{-2}$.d$^{-1}$ for sample (a), the permeation coefficients are between $0.11$ g. mm.m$^{-2}$.d$^{-1}$ (b) and $0.14$ g.mm.m$^{-2}$.d$^{-1}$ (c) for most of polyethylene samples studied. Polyethylene manufactured in Algeria...
Table 1: Experimental values of permeability and diffusion coefficients for different polymers

<table>
<thead>
<tr>
<th>Thickness L 10^4 cm</th>
<th>LDPE</th>
<th>Polyetherimide</th>
<th>Polyetheretherketone</th>
<th>Polyimide</th>
<th>PET</th>
<th>PES</th>
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<tbody>
<tr>
<td>0.10 mmol.cm^-1.s^-1</td>
<td>0.77</td>
<td>3.44</td>
<td>4.07</td>
<td>0.42</td>
<td>4.76</td>
<td>37.6</td>
</tr>
<tr>
<td>P Barrer</td>
<td>73</td>
<td>324</td>
<td>384</td>
<td>40</td>
<td>450</td>
<td>3550</td>
</tr>
<tr>
<td>D 10^11 cm^2.s^-1</td>
<td>7.42</td>
<td>0.66</td>
<td>0.73</td>
<td>0.10</td>
<td>0.56</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Table 2: Comparison of experimental values of LDPE permeability coefficients with those of the literature

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P 10^8 g.mm.m^-2.j^-1</td>
<td>0.31</td>
<td>0.11</td>
<td>0.14</td>
<td>0.12</td>
<td>0.06</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>38</td>
<td>25</td>
<td>21</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>

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REFERENCES